Annual Report for Michigan Great Lakes Protection Fund Grant

Title: Development of a Method for Predicting the Bioavailability and Mobility of Persistent and Bioaccumulative Toxic Contaminants in Great Lakes Sediments

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Purpose and Objectives

A fundamental goal of environmental risk assessment is reliable prediction of the ecological impacts of xenobiotic stressors. There is a growing body of information and observations indicating that hydrophobic organic compounds become less available to environmental receptors as the time of their sorptive association with geosorbents such as soils and sediments increases, the so called "aging" process. Current regulatory guidelines for cleanup and risk assessments of contaminated sites are based on total concentrations of toxic chemicals, however, and thus give little or no consideration to the more limited environmental availability of such chemicals when they are sequestered by soils or sediments. Current approaches can therefore significantly overestimate the hazards or risks associated with such "bound" chemicals, especially for aged chemicals at historically contaminated sites. Current methods for evaluating cleanup requirements for contaminated sites thus often lead to unnecessary expenditures of funds and resources. More realistic methods for assessing the potential risks in the Great Lakes of such organic contaminants associated with sediments, particularly those classified as persistent and bioaccumulative toxics (PBTs), are therefore essential for regulatory assessment and control.

The overall goal of this research is development of a rapid and readily applicable procedure for predicting the bioavailability and environmental mobility of sediment-associated contaminants. The procedure involves the use of an innovative technique we have developed for measurement of the sorption and desorption properties and behaviors of such contaminants. The proposed project has three specific objectives: (i) determine critical sorption/desorption and sequestration relationships for representative PBT compounds for a range of representative sediments from the Great Lakes system; (ii) determine the bioavailability of selected individual and mixed PBTs to

relevant aquatic organisms; and, (iii) develop quantitative interrelationships between sediment composition, PBT sorption/desorption behavior, and compound bioavailability.

Materials and Methods and Results

1) Sediment collection and characterization.

Three PAHs (phenanthrene, fluoranthene, and pyrene) purchased from Aldrich-Sigma (St. Louis, Mo) were used as representative PBT compounds. 3M Empore 47-mm C18 membrane [poly(tetrafluoranthylene) impregnated with a bonded octyl silica sorbent] were purchased Fisher Scientific Products. Tenax beads (60/80 mesh) were purchased from Alltech Associates (Deerfield, IL). All solvents were HPLC grade.

A culture of aquatic oligochaete (*Lumbriculus variegates)* was obtained from Carolina Biological Supply Co (Burlington, NC), was established using a procedure recommended by Dr. Peter Landrum of the Great Lakes Environmental Research Laboratory in Ann Arbor, MI. These organisms, which were used for determining the bioaccumulation potential of target PBT compounds associated with the sediments under investigation, were cultured in a 5-gallon aquarium containing dechlorinated tap water and unbleached brown paper towels. The overlying water was changed every 4-7 days and maintained at 22-23^{o}C. The aquaria were subjected to sequential 16:8 (light:dark) photoperiods and the worms were fed with worm food twice a week,

Twenty sediment samples were collected from various locations in Michigan and Ohio. The collection sites and the properties of these sediments are listed in Table 1. The sediments were sieved (1-mm screen size) and stored at 4^{o}C for further use.

Table 1. Sediment collection and characterization

Sediment	TOC	Background compound	Toxicity	pH	Collection
S1	ND[a]	++[b]	+[c]	ND	Pointe Mouillee, CDF, Site 1, Detroit River, MI
S2	ND	++	+	ND	Pointe Mouillee, CDF, Site 2, Detroit River, MI
S3	ND	++	+	ND	Pointe Mouillee, CDF, Site 3, Detroit River, MI
S4	ND	++	+	ND	Pointe Mouillee, CDF, Site 4, Detroit River, MI
S5	1.32	++	+	6.6	Saginaw River, MI
S6	0.46	-	-	7.8	Quanicassess River, MI
S7	0.97	-	-	7.8	Fish Port, MI
S8	0.03	-	-	8.0	Thomas Marina, MI
S9	ND	+	ND	ND	Gallup Park, Ann Arbor, MI
S10	0.00	+	+	7.9	Whitmore Lake, MI
S11	0.67	+	+	7.9	Huron River, Site 1, Ann Arbor, MI
S12	0.00	-	-	7.9	Anchor Bay, MI
S13	0.61	-	-	8.0	New Baltimore, MI
S14	ND	++	+	6.9	Protage Creek, MI
S15	0.00	++	ND	8.1	Fair Haven, MI
S16	6.45	+	-	7.3	Lyndon Pond, Chelsea, MI
S17	35.91	+	+	ND	Green Lake, MI
S18	1.09	-	-	7.8	Huron River, Site 2, Ann Arbor, MI
S19	0.00	+	+	7.7	Scouter River, Kalamazoo, MI
S20	2.57	++++	+	7.5	Little Scioto River, Marion, Ohio

a. ND: Not determined
b. +: contained trace of background compounds
c. +: toxic, -: non toxic

Total organic carbon (TOC) was determined using a Perkin-Elmer 2400-II Carbon-Hydrogen-Nitrogen (CHN) analyzer. As indicated in Table 1 (column 2), total organic carbon (TOC) contents ranged from 0.46 to 1.091% for five of the seven sediments found to contain sediment organic matter (SOM), while the sixth, the sediment from Lyndon pond, had an organic carbon content of 6.45%, and the organic carbon content of the seventh sediment from Green Lake was

35.91%. The other sediment samples did not contain any SOM. The pH values of the water overlying the sediments were measured and found to ranged from 7.3 to 8.1 (Table 1, column 5).

Sediment samples were extracted with methanol and dichloromethane under sonication conditions, and background concentrations of PAHs were determined using HPLC. The results given in Table 1 reveal that six of the 20 sediments contained no measurable trace of any of the target contaminants, six had trace amounts of PAHs, and eight were heavily contaminated with phenanthrene, anthracene, fluoranthene, pyrene, benzanthracene, dibenzoanthracene, benzo(*k*)fluoranthene, and benzo(*a*)pyrene. Total concentrations of PAHs for most of the contaminated sediments ranged from 13.4 ppm to 57.8 ppm. The sediment from the Little Scioto River in OH (S20) was the exception, with a total PAH concentration greater than 1520 ppm.

Twelve of the sediment samples that contained no measurable or only trace levels of target compounds were examined to assess their toxicity to aquatic worms, i.e., *L. variegates*. Sediment samples (50g, dry weight) were added to 600-ml glass beakers, mixed with dechlorinated tap water, and allowed to settle for 24 h. Adult aquatic worms were then added to each beaker (10 worms per beaker) and exposed for 4-10 days at 23^{o}C and a 16:8 (light:dark) photoperiod sequence. The results revealed no reductions in the number of worms for any of the samples tested, indicating no toxic effects of these twelve sediments for this organism. The worms were found to burrow selectively into six of the twelve sediments, and these six were down-selected for use in further experiments.

The six sediments that showed no trace of target compounds and no toxicity to aquatic oligochaete based on the above characterizations and measurements (sediments S6, S7, S8, S12, S13, and S18) were designed as “clean”, and used as such in further experiments involving PBT spiking to measure mobility and bioavailability of target compounds. The field-contaminated sediment collected from the Little Scioto River was used for subsequent desorption tests.

2) Sediment spiking and aging.

Phenanthrene, fluoranthene, and pyrene were spiked individually to the six clean sediments at various solution phase concentrations. The test compounds were dissolved in acetone, added to 2-L glass reactors, and allowed to spread on the glass walls. After the acetone was evaporated in a hood, the selected sediments were added to the glass jars and mixed with Huron River water for one week. The equilibrated solutions were then stored at 4^{o}C to allow the extended sediment-contaminant aging process to occur.

After these solutions of test compounds were aged with the selected sediments (phenanthrene for 104 days, fluoranthene for 58 days, and pyrene for 74 days), the remaining overlying water was decanted from the reactors. Fresh clean water was added to the reactors and the aged sediment slurries were mixed for two days, after which the water was separated from the solid phase by sedimentation and the overlying water decanted. Each aged sediment sample was then freeze-dried and thoroughly mixed. These sediments were subsequently used for measuring the desorption of test compounds and their bioavailability (uptake) to aquatic oligochaetes.

3) Bioavailability of PAHs to aquatic oligochaetes.

To measure the bioavailability of sediment-sorbed PAHs, samples of the freeze-dried contaminated sediments (50 g) were transferred into 600-ml glass beakers and Huron River water (400ml) was added to each. After the sediment has settled for 24 hrs, triplicate groups of adult *L. variegates* (40 worms each) were placed in the glass reactors and maintained at 23^{o}C under 16:8 (light:dark) alternating photoperiod for 14 days, half of the overlying water in each reactor was changed every two days. At the conclusion of the 14-day exposure period, the test worms were collected from the sediments using a 355-mm screen size sieve and transferred into glass tubes containing clean water for 24 hours for gut purging, then carefully blotted dry and weighed.

Desorption under ambient conditions.

Aqueous desorption rates of aged phenanthrene, fluoranthene, and pyrene in sediments were determined using C18 membrane disks or Tenax beads to create infinite-sink desorption conditions. Triplicate sediment samples (0.5-1.0 g) were transferred into 35-ml glass centrifuge tubes, and a 0.01-M $CaCl_2$ aqueous solution containing NaN_3 was added to each centrifuge tube to a nearly full condition to minimize volatilization losses. C18 membrane disks were cut into two or four pieces and conditioned with methanol and water. They were then added to the slurry mixture to rapidly adsorb test compounds as they were released from the sediments into the water phase, thus maintaining near-zero water phase concentrations of the compounds at all times. The tubes were sealed with Teflon-lined caps and mixed on an end-over-end shaker for different predetermined periods of time. At the end of each predetermined time period, the membrane was removed, rinsed with deionized water, dried in a paper towel, and then transferred to a 10-ml glass vial. Methanol was added to elute the PAHs from the membrane disks and the extracts were analyzed for the test compounds using HPLC.

4) Desorption of PAHs from a field contaminated sediment in superheated water

The desorptions of aged PAHs from spiked and field-contaminated sediments were also measured using a novel superheated water technique (SWAT). Desorptions at 100^{o}C for spiked sediments and desorption at 75, 100, 150, and 200 ^{o}C for field-contaminated sediments were conducted in superheated water. The SWAT desorption system involved the pumping of helium-purged distilled and deionized water through then through a preheat coil and a stainless steel reactor containing 1- 2g sediment samples in a Varian 2700 gas chromatograph oven at a rate of 1.0 ml/min. The hot water containing the desorbed compounds exited the oven, passed through a cooling coil and was depressurized via a back pressure regulator. Cooling coils and back pressure

regulators were constantly flushed with methanol at a 1:2 methanol: water volume ratio via a second pump and a mixing "T" at the oven exit. Tubing was 0.0625 in. o.d. by 0.02 in i.d. stainless steel. Back pressures of 5 and 20 atm were applied for the 150^{o}C and 200^{o}C desorptions, respectively, to avoid conversion of liquid water to steam. The extracts were collected sequentially under ambient temperature and pressure conditions in glass jars and stored at 4^{o}C prior to analysis. For very low target compound levels, C18 membrane disks conditioned with methanol and Milli-Q water were added to the collected solutions that did not contain methanol to recover the test compounds, and the test compounds then eluted with methanol. All collected samples were analyzed for both the amount of each test compound desorbed and the total amount in the sediment.

5) Extraction and chromatographic analysis

Sediment and worm samples were placed in 35-ml glass centrifuge tubes and an appropriate amount of methanol was added to each tube. The tubes were extracted in an ultrasonic water bath for four hrs and then mixed on a vortex. The slurry was centrifuged at 3000 rpm for 15 min. The supernatants (~1 ml) were transferred to autosample vials. The preliminary test showed that extraction by sonication provided a recovery similar to that of a Soxhlet extraction.

The concentrations of target compounds in the extraction solution were determined using a liquid chromatograph (model 1100, Hewlett-Packard) equipped with a quaternary gradient pump, diode array and programmable fluorescence and UV detectors and an autosampler. The analysis was performed with a C18 column and an acetonitrole/water mixture as mobile phase at a flow rate of 0.8 ml/min.

Results

1). Concentrations of target compounds in sediments

The concentrations of PAHs remaining in the spiked and aged sediment samples are reported in Table 2. Phenanthrene concentrations varied greatly among the five sediments, ranging from 4.56 to 74.78 μg/g. Concentrations of fluoranthene and pyrene were much higher, ranging from 100.81 to 140.23 μg/g for fluoranthene and from 118.51 to 204.10 μg/g for pyrene. The concentrations of seven representative PAH compounds of the more than ten found in the Little Scioto River sediment are listed in Table 3.

Table 2. Concentrations of phenanthrene, fluoranthene, and pyrene in aged sediments

	Concentration (μg/g sediment)		
Sediment	Phenanthrene	Fluoranthene	Pyrene
S6	4.56	129.71	192.36
S7	5.87	100.81	204.10
S8	74.78	143.33	150.32
S12	Not spiked	132.45	186.53
S13	7.11	140.23	118.51
S18	34.50	130.36	143.06

Table 3. PAH concentrations (μg/g) in the Little Scioto River sediment

Compound	Conc. (μg/g)	Compound	Conc. (μg/g)
Phenanthrene	526.30	Anthracene	165.50
Fluoranthene	366.70	Pyrene	198.92
Chrysene	47.53	Benz(e)anthracene	65.98
Benzo(k)fluoranthene	44.35		

2). Bioavailability of test compounds

Measurements were made to determined the effect of time of exposure of aquatic worms to sediments containing pyrene or phenanthrene on the uptake of these two compounds. For this purpose, samples of the Fish Port sediment were aged with two test compounds, pyrene for 58 days at 31.71 μg/g and phenanthrene for 92 days at 5.78 μg/g. Aquatic worms were exposed to these contaminated sediment samples for periods of up to 28 days. As indicated respectively in Figures 1 and 2 for phenanthrene and pyrene, the amount and percentages of the two compounds bioaccumulated increased monotonically for the first 14 days and then began to decline, perhaps because of transformation of the test compounds by the aquatic worms. Given these uptake rate results a 14-day time period was selected for subsequent bioavailability measurements.

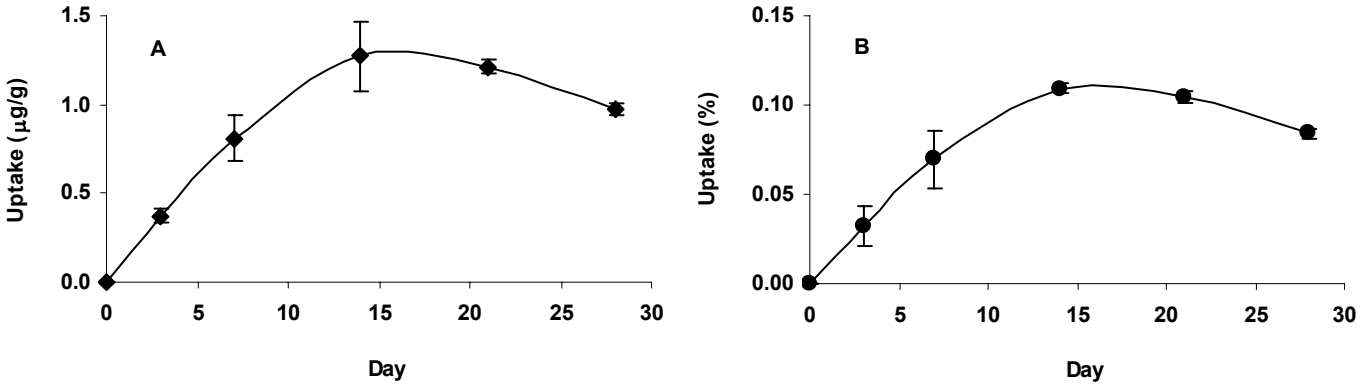

Figure 1. Effect of time of exposure on the uptake of phenanthrene from the Fish Port sediment by aquatic oligochaete, *L. variegates*.

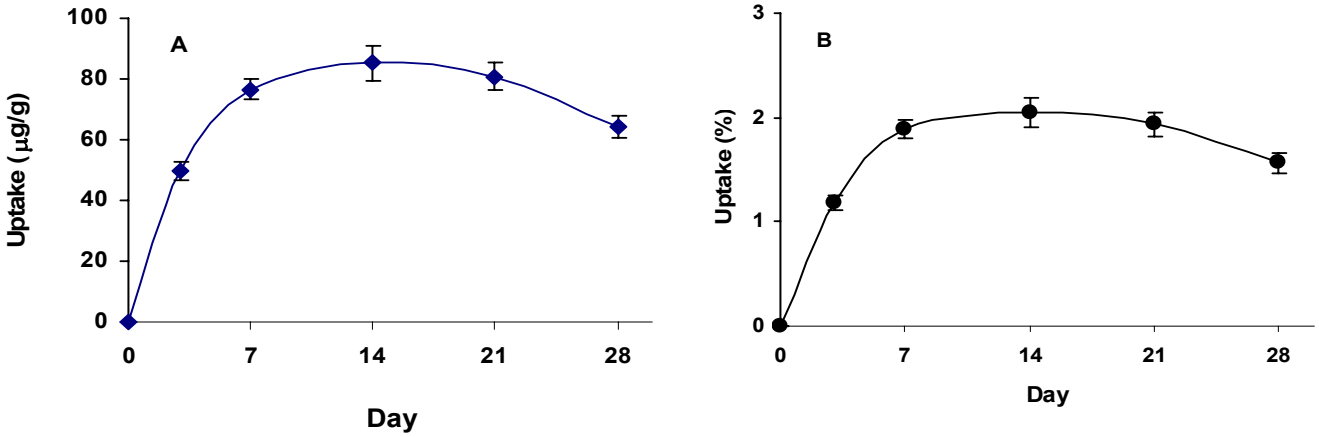

Figure 2. Effect of time of exposure on the uptake of pyrene from the Fish Port sediment by aquatic oligochaete, *L. variegates*

The uptakes of phenanthrene, fluoranthene, and pyrene by aquatic worms from six aged sediments over 14-day exposure periods were also determined, and the results are summarized in Table 4. Aquatic worms were exposed to the contaminated sediment samples. The test compounds from the worm bodies were extracted using the methanol/sonication technique, and the concentrations of these extracts analyzed by HPLC. As noted in Table 4, the amounts of these compounds bioaccumulated by worms varied among the different sediments tested. The uptake of phenanthrene was generally much lower than that of fluoranthene and pyrene. This might be attributed to the long aging time for phenanthrene and its lower concentrations in the sediments.

Table 4. Uptakes of phenanthrene, fluoranthene, and pyrene by *L. variegates* from different sediments

	Phenanthrene		Fluoranthene		Pyrene	
Sediment	(μg/g)	(%)	(μg/g)	(%)	(μg/g)	(%)
S6	7.27	0.044	243.38	0.462	205.59	0.223
S7	9.83	0.039	351.31	0.857	233.38	0.239
S8	20.35	0.007	524.08	0.899	232.32	0.326
S12	ND[a]	ND	779.63	1.448	271.91	0.287
S13	6.82	0.025	39.87	0.070	22.35	0.039
S18	43.75	0.045	447.88	0.845	217.33	0.299

a: Not determined.

Table 5 summarizes the effects of pyrene concentrations in sediments on the uptake of this representative PAH by aquatic worms. Pyrene was first aged with the Fish Port sediment at five different concentrations for 45 days, and the aquatic worms then exposed to the aged sediment samples for 14 days. The mass amount of pyrene taken up by the aquatic worms increased in an

essentially linear manner with increased concentrations in the sediment (correlation coefficient of $R^2 = 0.995$), while the uptake percentage remained fairly steady because of the small total mass of the aquatic worms involved.

Table 5. Effects of initial sediment concentrations (IAS) on the uptake of pyrene by *L. variegates* from the Fish Port sediment.

IAS (μg/g)	Uptake	
	μg/g	%
2.79	10.92	3.25
30.44	79.48	2.17
42.27	118.30	2.33
57.59	138.98	2.01
98.50	242.76	2.05

3). Desorption rates of spiked PAH compounds

The aqueous phase desorption behaviors of phenanthrene and pyrene from laboratory spiked sediments under ambient temperatures (22°C) with C18 membrane disks and at different elevated temperatures under superheated conditions were characterized by the following a three-parameter, two-component, first-order rate model

$$\frac{C_t}{C_0} = \phi_s \exp(-k_s t) + (1-\phi_s)\exp(-k_r t) \qquad (1)$$

The term in Equation 1 C_0 is the initial amount of chemical sorbed in the sediment, C_t is the concentration of chemical in sediment at time *t*, ϕ_s is the fraction of chemical which is slowly released from a sediment, 1- ϕ_s is the fraction of chemical which is rapidly released, k_s is a first-order rate constant for the slowly released fraction, k_r is a first-order rate constant for the rapidly

released fraction. The desorption parameters were determined by fitting the desorption rate data with Equation 1 using the Levenberg-Marquardt nonlinear regression techniques (SAS Institute Inc., Cary, NC).

The desorption patterns of both PAHs, shown in Figures 3 and 4 respectively, manifest two-stage behavior, i.e., a rapid stage and a slow stage. It is evident that in all cases desorption into superheated water at 100^{o}C is much faster than that at 22^{o}C. For example, the desorption of pyrene in superheated water plateaued after only 8-10 hours for most of the aged sediments, while no plateau had been reached for any of the sediments after 54-day periods of desorption at ambient temperature. The results also show that desorption rates under both elevated temperature and ambient conditions were fitted well in all cases using the rate model given in Equation 1. The parameters for the best fit of this rate model for each data set are given in Table 5. While the desorption rates were in all cases much faster using the SWAT procedure, the breakout of the slowly desorbing fractions obtained from model fits of the data for the two different desorption procedures were similar for each sediment tested. This is evident by comparing the ϕ_s values in Table 5 and noting the strong correlation for ϕ_s given in the first part of Figure 5. Similarly, inspection of Table 6 and the second part of Figure 5 (B) reveal strong correlations between values for the total amount desorbed (TAD) determining using 100^{o}C SWAT and 22^{o}C C18 membrane procedures.

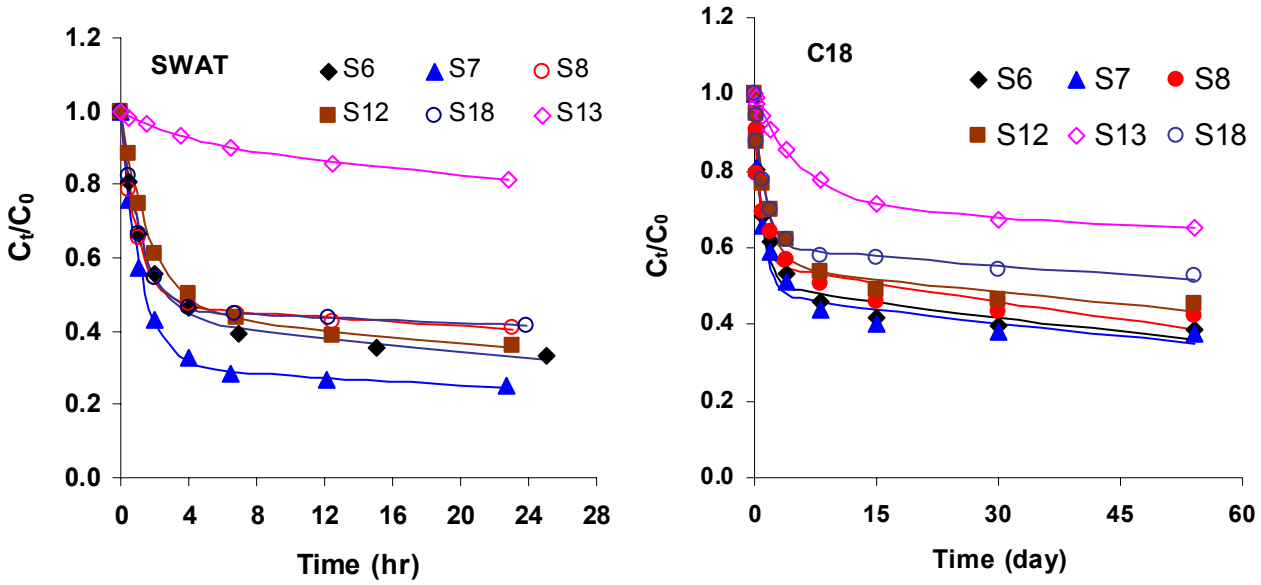

Figure 3. Desorption of pyrene from six aged sediments at 100°C with superheated water and at ambient temperature in an infinite-bath reactors using a C18 membrane

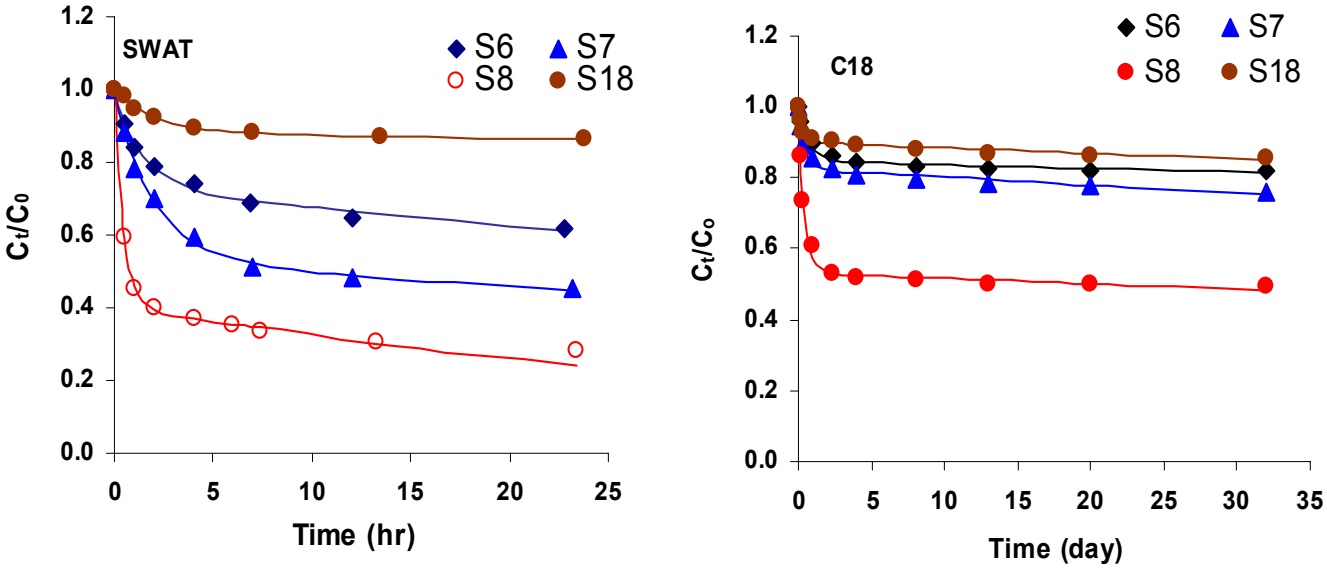

Figure 4. Desorption of phenanthrene from four aged sediments at 100°C with superheated water and at ambient temperature (22°C) with a C18 membrane in an infinite-bath reactor

Table 6. Desorption model parameters and total amounts desorbed (TAD) for pyrene and phenanthrene during test periods for different sediments under mild superheated water and ambient temperature conditions

	SWAT (100°C)				C18 Membrane (22°C)			
Sediment	ϕ_s	k_s (hr^{-1})	k_r (hr^{-1})	TAD (μg/g)	ϕ_s	k_s (day^{-1})	k_r (day^{-1})	TAD (μg/g)
				Pyrene				
S6	0.426	0.0130	0.8181	126.48	0.506	0.0063	1.0200	115.71
S7	0.279	0.0103	0.8271	158.13	0.475	0.0065	1.0298	129.38
S8	0.512	0.0068	1.0327	83.93	0.563	0.0059	0.6545	86.91
S12	0.455	0.0108	0.5672	119.56	0.562	0.0037	0.1754	102.20
S13	0.917	0.0054	0.2868	20.49	0.727	0.0010	0.7695	40.92
S18	0.425	0.0039	0.8749	87.76	0.592	0.0036	0.8131	67.79
				Phenanthrene				
S6	0.733	0.0081	0.7508	1.74	0.849	0.0014	1.4736	0.74
S7	0.541	0.0084	0.5367	3.83	0.826	0.0029	2.4883	1.43
S8	0.407	0.0227	2.3023	54.26	0.534	0.0029	2.3746	37.75
S18	0.882	0.0008	0.4908	4.61	0.899	0.0017	3.3894	4.88

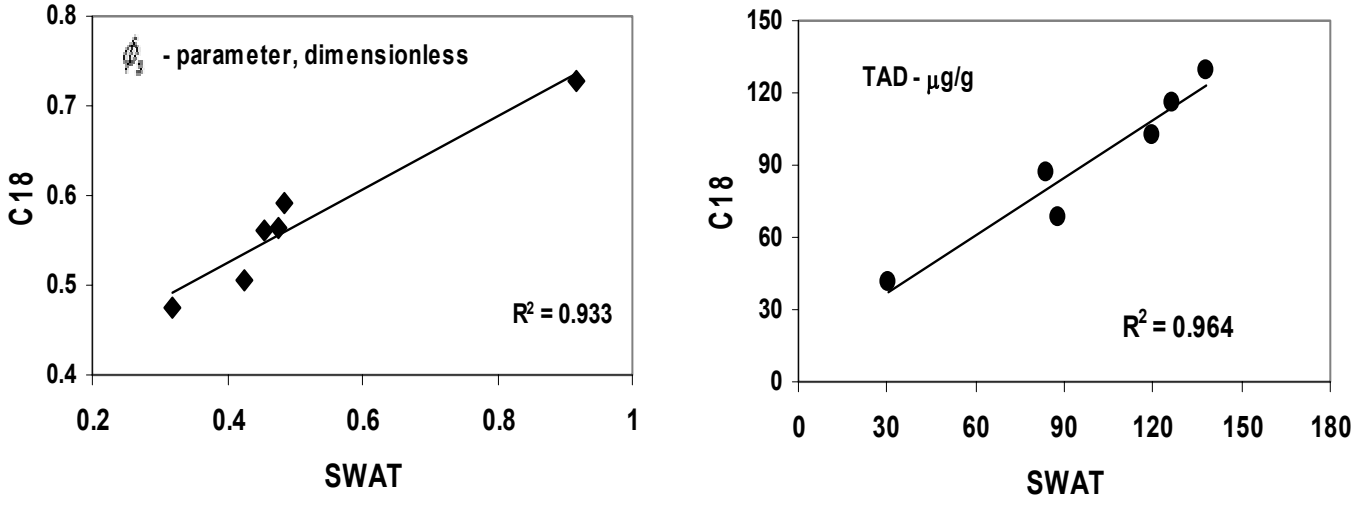

Figure 5. Correlations between desorption parameters for pyrene from different sediments determined using the 100°C SWAT procedure and the 22°C C18 ambient temperature procedure

Aqueous phase desorptions of pyrene from Fish Port sediment spiked at five different concentrations were also determined under both superheated water and ambient temperature. The results, shown in Figure 6, reveal that the desorption rates are again fitted well for both procedures with the rate model given in Equation 1, again demonstrated the much faster desorption rates obtained and shorter asses periods required using the SWAT procedure. Table 7 and Figure 7 again show good correlations between values of ϕ_s and TAD determined by the SWAT and C18 procedures.

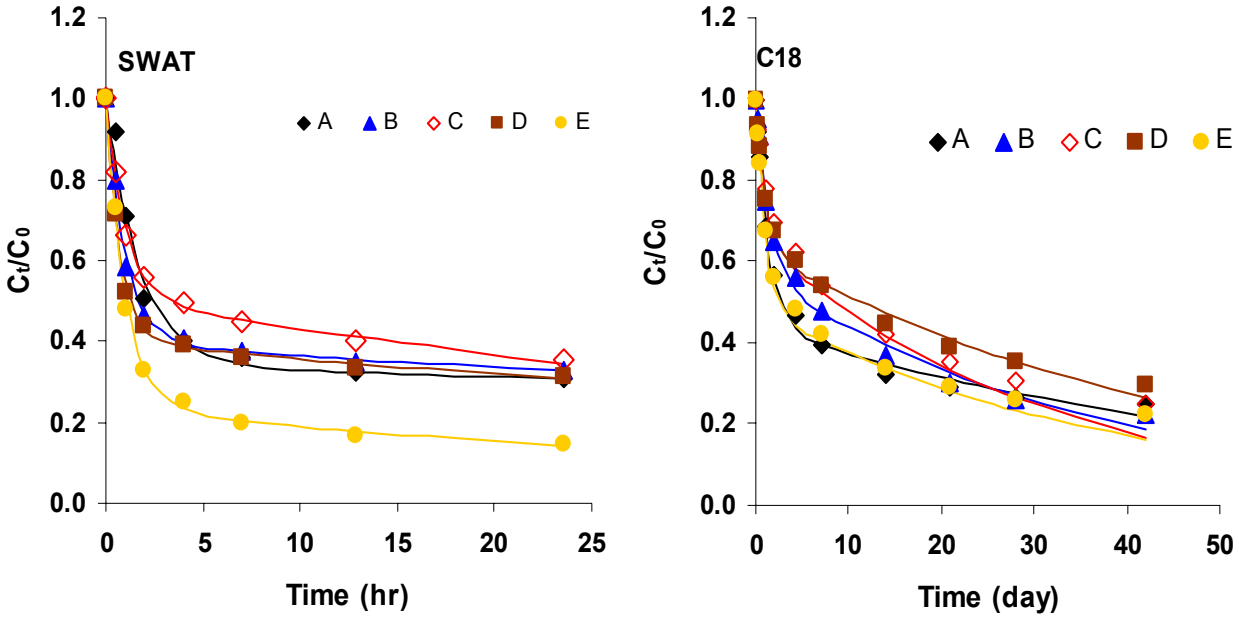

Figure 6. Desorption of pyrene from six aged sediment at 100°C with superheated water and ambient temperature (22°C) with a C18 membrane (Spiking concentrations: A= 2.79 μg/g; B= 30.44 μg/g; C= 42.27 μg/g; D=57.59 μg/g and E=98.50 μg/g)

Table 7. Desorption model parameters and total amounts desorbed (TAD) for pyrene desorbed during test periods from the Fish Port sediments at five concentrations under mild superheated and ambient temperature conditions

	SWAT (100°C)				C18 Membrane (22°C)			
Sediment	ϕ_s	k_s (hr^{-1})	k_r (hr^{-1})	TAD (μg/g)	ϕ_s	k_s (day^{-1})	k_r (day^{-1})	TAD (μg/g)
2.79	0.337	0.0041	0.5611	1.94	0.484	0.0171	0.6756	2.10
30.44	0.396	0.0082	1.0071	20.39	0.568	0.0264	0.7281	23.60
42.27	0.511	0.0177	1.0048	29.09	0.662	0.0330	0.9819	29.84
57.59	0.398	0.0112	1.3809	35.94	0.630	0.0205	0.9326	44.18
98.50	0.240	0.0233	0.9927	87.04	0.488	0.0262	0.9713	75.47

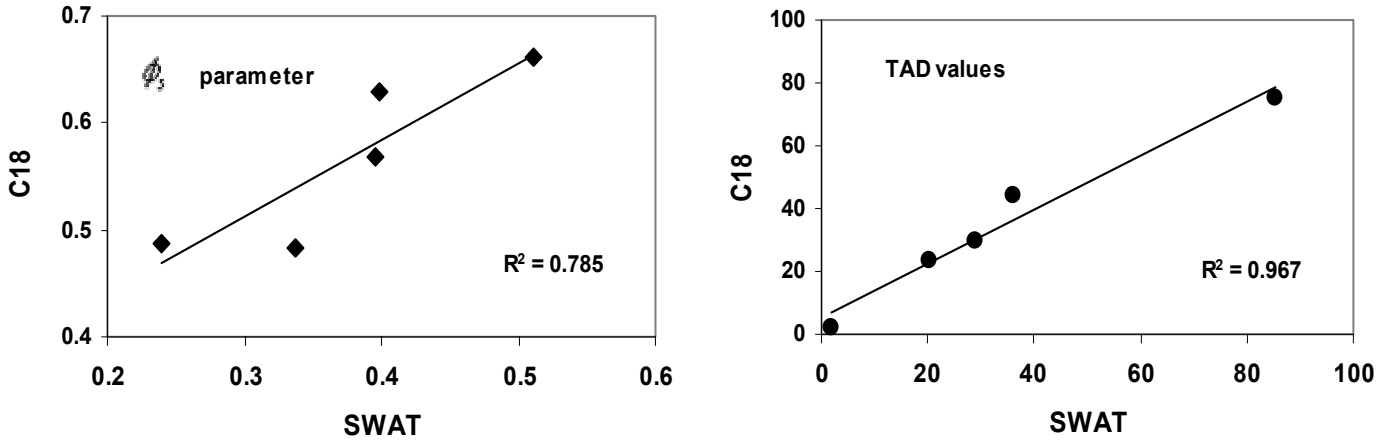

Figure 7. Correlations between desorption parameters for pyrene from the Fish Port sediment at different concentrations determined using 100°C SWAT procedure and 22°C C18 ambient temperature procedure

As shown by the data presented in Figure 8, no significant correlation was found between the amounts of pyrene assimilated by aquatic worms and the amounts desorbed from the six different sediments identified in Table 3. This is not unexpected, given the different properties of these six

sediments. More specifically, it can not be expected that the relative ratios of desorption at 14 days (the biotest exposure period) to TAD are going to be similar for different sediments. However, strong correlations were found between biological uptake of pyrene and its TAD under both superheated water and ambient temperature conditions when aquatic worms were exposed to the Fish Port sediments spiked and aged at five different pyrene concentrations. Each experiment was in this case performed with exactly the same sediment and it can be expected therefore that the relative ratios of desorption at 14 days to TAD are going to be similar. This in turn would be expected to yield good correlations between TAD and bio-uptake values. It is evident from these results that existing measures of total contaminant load are likely to have little relationship to actual contaminant bioavailability, and that further studies are therefore needed to develop a more sediment-specific bioassay methodology for remedial and regulatory actions.

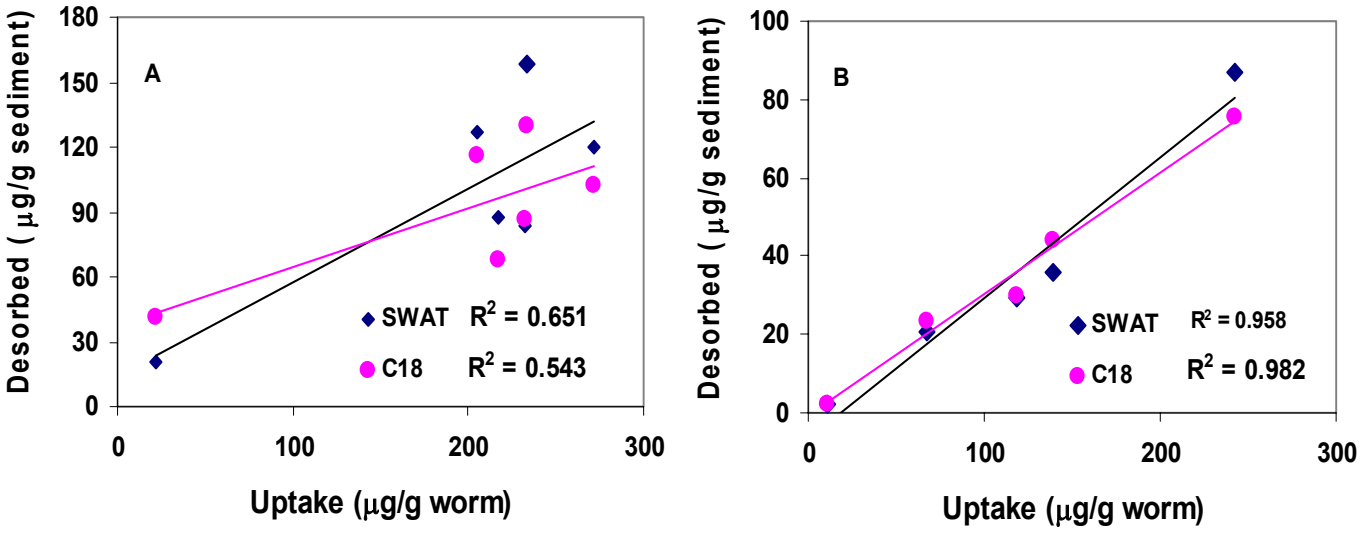

Figure 8. Correlations between uptake of pyrene by aquatic worms and its desorption from six different sediments (A) and from Fish Port sediment spiked to give different IAS levels (B)

4). Desorption of PAHs from field contaminated sediment under various heated, superheated, and ambient temperature conditions

The aqueous desorption characteristics of PAHs from the field-contaminated LSR sediment (S20) were determined using the SWAT technique at different temperatures, and the results were compared to long-term aqueous phase desorption measurements at ambient temperatures using Tenax beads to create infinite-sink desorption conditions. As illustrated in Figure 9, the desorption of PAHs from the LSR sediment increased with increasing temperatures, the rates of low-molecular-weight PAHs desorption being much faster than those of high-molecular-weight PAHs. At 75^{o}C the desorptions of only four low-molecular-weight PAHs were observed over a test period of 72 hrs, with no desorption plateau being obtained over that period of time. When the temperature was increased to levels of 100^{o}C, 150^{o}C and 200^{o}C, the desorptions of three high-molecular-weight PAHs were also detected. The desorption of the four low-molecular-weight PAHs reached near-plateau values in 72 hr at 100^{o}C, and the desorptions of the three high-molecular-weight PAHs reached plateaus within 24 hr at a desorption temperature of 200^{o}C. In stark comparison, the desorptions of all seven PAHs failed to reach plateau levels over a 205-day test period at ambient temperatures (22^{o}C), although desorption of the low-molecular-weight PAHs proceeded much faster than that of the high-molecular-weight PAHs.

It is evident from the solid lines in Figure 9 and 10 that the PAH desorption rate data for the LSR sediments were in all cases characterized well under ambient, heated and superheated water conditions using the desorption rate model given in Equation 1. Strong correlations were found to exist between the ambient desorption tests using Tenax beads and the desorption tests conducted in superheated water with correlation coefficient (R^2) values of 0.909, 0.992 and 0.942, respectively, for temperatures of 100^{o}C, 150^{o}C, and 200^{o}C

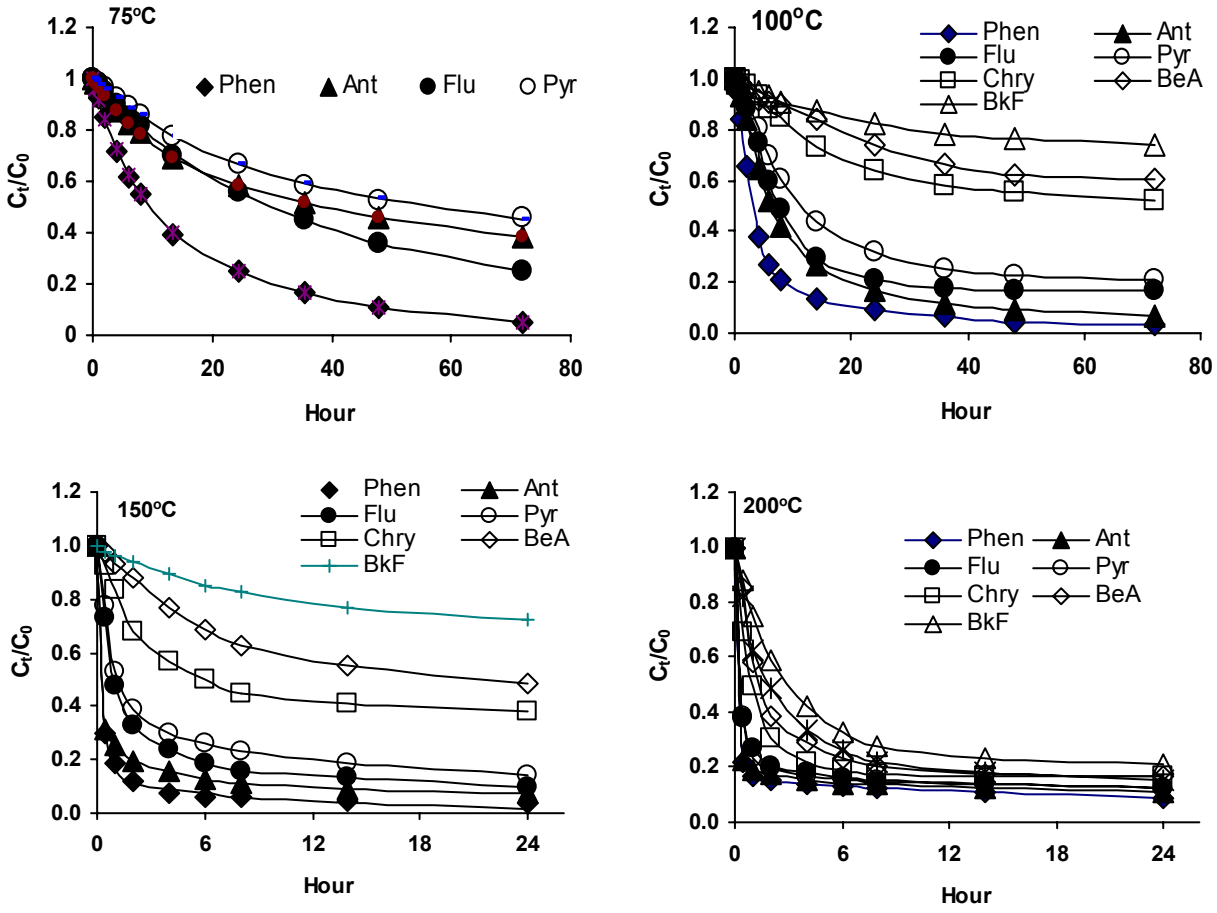

Figure 9. Desorption of PAHs from LSR sediment by superheated water at different temperatures

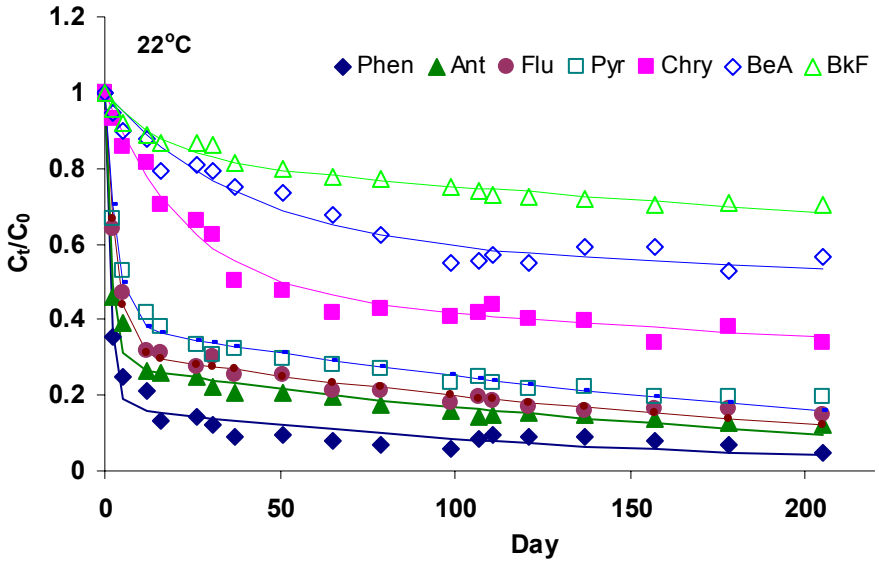

Figure 10. Desorption of PAHs from LSR field-contaminated sediment at ambient temperature

Conclusion

An accelerated superheated water desorption technique (SWAT) was developed and optimized to measure the desorption/release of hydrophobic organic chemicals (HOCs) into aqueous phase from sediments. The aqueous phase desorptions of seven PAH compounds, i.e., phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzanthracene, and benzo(*k*)fluoranthene, from both laboratory spiked and field-contaminated sediment samples were determined at elevated temperatures using SWAT procedure and at ambient temperatures using C18 membrane disks and Tenax beads. The aqueous desorptions of these compounds under both SWAT and C-18 conditions included a rapid stage and slow stage, and their patterns were characterized well with a three-parameter, two-component, first-order desorption rate model. The desorptions of the test compounds were much faster using SWAT procedure than that the ambient C-18 procedure. Strong correlations were found between the desorptions of the test compounds using the two different procedures. Due to the different properties of sediments tested, the desorption and bioavailability of the organic compounds sorbed by these sediment samples to aquatic worms were quite different from each other. It is not unexpected that no significant correlation was found between the amounts desorbed over the entire course of the test (i.e., TAD values) and the amounts assimilated by worm during 14-day exposure periods. However, strong correlations were found between the biological uptake of pyrene and its TAD under both superheated water and ambient temperature conditions when the aquatic worms were exposed to the same sediment samples spiked and aged at five different pyrene concentrations. Such correlations are expected because the contaminant desorption patterns and availability to aquatic worms are expected to be similar for the same sediment under different loading conditions.

This study has demonstrated that the SWAT technology provides a unique and very promosing means for rapid assessment (i.e., hours or days) of the normally very slow desorption/release rates of sorbed organic contaminants from soils and sediments, processes that normally occur over periods of years at ambient environmental temperatures. Further studies are needed to draw more conclusive parallels between the desorption behaviors and bio-uptake processes of target contaminants. There is clear evidence from the work reported here that such parallels would lead directly to the development of predictive relationships between the rapid SWAT desorption test measurements and the actual bioavailability of persistent toxic organic contaminants in sediments.